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A correlation between crystal structure and catalytic activity in the solid solutions $CdMo_xW_{1-x}O_4$

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Abstract

Two $CdMo_xW_{1-x}O_4$ solid solutions with the scheelite and the wolframite structures were synthesised via different techniques and their structures were determined from powder refinements. The limit of the reciprocal solubility of Mo in $CdWO_4$ has been checked. Several compositions of the solid solutions have been tested in the catalytic mild oxidation of propane or propene and relations between the structures and the catalytic activity are proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; $CdMo_xW_{1-x}O_4$; Catalytic activity; Powder refinements; Mild oxidation

1. Introduction

Metal molybdates and tungstates represent a very relevant class of inorganic phases useful in the field of heterogeneous catalysis [1–3]. Industrial catalytic formulations for propylene oxidation to acrolein are based on multicomponent metal oxides containing very often molybdenum as in the case of Bi–Mo–O phases [4–7]. From fundamental investigations, it appears that this reaction is structure-sensitive: when molybdenum tetrahedra or octahedra are isolated the catalysts are rather inactive, whereas when Mo entities form long chains the catalysts are active but CO_2 is mainly produced [8,9]. Good activity and selectivity seem to occur for ensembles of two or three metal transition octahedra [10]. Catalysts containing W have been studied much less.

The aim of the present study is to compare the activity of solids containing either Mo or W, or both elements. The chosen compounds are of $CdMO_4$ (M=Mo, W) type and they comprise of the $CdMo_xW_{1-x}O_4$ solid solutions recently discovered [11]. The study has been extended to propane oxidation, a much more difficult reaction which can lead to propylene and/or acrolein.

2. Experimental

Powder samples $CdMo_xW_{1-x}O_4$, with x=0, 0.125, 0.25, 0.5, 0.75, 1, were prepared via hydrothermal synthesis in a Teflon-lined autoclave, adding 2 cm^3 of water and 5% in weight of a salt like NaF, KF and KCl to the stoichiometric mixture of the oxide precursors. The temperature cycle consisted of a heating ramp 50 $K\,h^{-1}$, an isothermal heating at 473 K for 48 h, a cooling rate of 1 $K\,h^{-1}$ until 423 K and a final cooling rate to room temperature, at a speed of 3 $K\,h^{-1}$. Other powders, also suitable for catalytic tests, have been prepared by a classical co-precipitation method, starting from nitrate precursors.

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Table 1
Rietveld main parameters of some refined structures

Atom	Position	x	y	z	B (Å^2)	Occupancy	Bragg factors
$CdWO_4$ S.G. P2/c							
W	2e	0	0.25	0.1784(3)	0.24(4)	0.5	R=5.36%
Cd	2f	0.5	0.75	0.3020(5)	0.46(9)	0.5	R_p=7.34%
O1	4g	0.189(2)	0.454(3)	0.901(2)	1	1	R_{wp}=11.1%
O2	4g	0.250(2)	0.393(3)	0.360(2)	1	1	χ^2=4.23%
$CdMoO_4$, S.G. $I4_1/a$							
Mo	4a	0	0.25	0.125	0.41(3)	0.25	R=6.71%
Cd	4b	0	0.25	0.625	0.10(3)	0.25	R_p=12.9%
O	16f	0.240(2)	0.091(2)	0.0421(9)	1	1	R_{wp}=19.2%
$CdMo_{0.025}W_{0.75}O_4$, S.G. P2/c							
W	2e	0	0.25	0.1760(7)	0.62(1)	0.375	χ^2=5.96%
Mo	2e	0	0.25	0.1760(7)	0.62(1)	0.125	R=4.83%
Cd	2f	0.5	0.75	0.2991(9)	0.5	0.5	R_p=8.71%
O1	4g	0.181(4)	0.443(7)	0.919(4)	1	1	R_{wp}=11.7%
O2	4g	0.240(4)	0.416(8)	0.381(4)	1	1	χ^2=2.31%
$CdMo_{0.75}W_{0.25}O_4$, S.G. $I4_1/a$							
Mo	4a	0	0.25	0.125	0.68(2)	0.1875	R=3.95%
W	4a	0	0.25	0.125	0.68(2)	0.0625	R_p=10.9%
Cd	4b	0	0.25	0.625	0.55(1)	0.25	R_{wp}=15.4%
O	16f	0.242(3)	−0.592(2)	0.042(1)	1	1	χ^2=5.46%

The BET surface areas of the catalysts are $<5\,m^2\,g^{-1}$ for solid state synthesis and about $24\,m^2\,g^{-1}$ for materials produced via soft chemistry. The patterns of the samples have been recorded with a Philips 1701 X-ray powder diffractometer (Cu Kα radiation, Ni filter, 45 kV, 35 mA). Structural calculations have been performed by the Rietveld-type profile refinement computer program FULLPROF [12]. The relevant parameters are summarised in Table 1.

The IR and FIR spectra were recorded by a Nicolet Magna 750 Fourier transform instrument. The FT-Raman spectra were recorded using a Brucker FTS100 (Nd-YAG laser). The skeletal spectra in the region above $400\,cm^{-1}$ have been recorded with KBr pressed disks and with a KBr beam splitter, while those in the far infrared region (400–50 cm^{-1}) have been recorded using the powder deposited on polyethylene disks, and with a “solid substrate” beam splitter. The catalytic experiments have been carried out in a fixed bed flow Pyrex microreactor, under atmospheric pressure, in the temperature range 570–725 K. The catalyst loading was a 0.5 g of granules in the size range 0.16–0.3 mm. The catalyst was heated up to 570 K in the stream of reactants for 2 h, then the temperature was gradually raised to 725 K. The catalytic activity analyses were successively performed at 45 min intervals. The feed was a mixture of C_3H_8 or C_3H_6–O_2 diluted with N_2, with a molar ratio $C_3H_8/O_2=3$ or $C_3H_6/O_2=0.5$ to realise a W/F contact time of 3.50 and $1.06\,g\,h\,l^{-1}$, respectively.

3. Results

3.1. Catalytic measurements

Catalytic measurements have been performed on fine powders obtained by hydrothermal or co-precipitation synthesis. No difference due to the two techniques has been observed in reactivity. Results are reported in Tables 2 and 3.

It appears that the conversions are quite low, explaining why so high a reaction temperature (725 K) has been selected. It has been checked that under the same conditions, no products are formed without any catalysts. The low activity could be ascribed to the cation Cd^{2+} chosen for this study. However, its redox properties and influence on its surrounding have

Table 2
Catalytic results of the mild oxidation of propane at 723 K

Catalyst	Conversion (%) for C_3H_8	Selectivity (%)				Balance
		C_3H_6	Acrolein	CO	CO_2	
$CdWO_4$	<1	–	–	–	–	–
$CdMo_{0.125}W_{0.875}O_4$	9	32	1	23	44	–
$CdMo_{0.25}W_{0.75}O_4$	9	39	2	15	36	8%
$CdMo_{0.5}W_{0.5}O_4$	<1	–	–	–	–	–
$CdMoO_4$	<1	–	–	–	–	–

already been studied in comparison with other cations (Ca, Pb, Ba) [8]. The results showed that cadmium structure presents rather good activity and selectivity in acrolein [8]. In order to find out the leading phenomenon in the reactivity change versus composition and to discover whether this depends on structural properties, we have performed a finer structural characterisation.

3.2. Structural characterisation

The structural characterisation of the mixed oxides has been performed either by X-ray diffraction (on single-crystals and powders) or by FT-IR bulk analysis. It is known that molybdates and tungstates of relatively big bivalent cations crystallise in the so-called scheelite structure (scheelite=$CaWO_4$) where molybdenum or tungsten exhibit a tetrahedral coordination [13].

Scheelite-type tungstates and molybdates of the same divalent metal are mutually soluble in the entire compositional range [14–16]. Alternatively, tungstates and molybdates of smaller bivalent cations can take the alternative wolframite structure (wolframite=(Fe,Mn)WO_4), where tungsten and molybdenum exhibit an overall sixfold coordination. Cd^{2+} compounds sit on the borderline so that the molybdate takes the scheelite structure while the tungstate takes the wolframite structure.

The accurate structural study of these mixed oxides has shown that for $0.50 \leq x \leq 1$ a monophasic domain of the $CdMoO_4$ scheelite type is obtained, while for $0 \leq x \leq 0.25$ the $CdWO_4$ wolframite structure is formed; for $0.25 < x < 0.50$, a gap of miscibility is manifested. In the first case a regular tetrahedral coordination for Mo and W is constituted, whereas in the second case the structure consists of waving chains of edge-sharing octahedra of W^{VI} and Mo^{VI} (the last within the limit of 20–25%). In Fig. 1, the experimental and simulated XRD patterns for the wolframite-type $CdMo_{0.25}W_{0.75}O_4$ compound are reported. A spectroscopic characterisation has been made using both FT-IR (resulting spectra are reported in Fig. 2) and Raman.

The interpretation of the spectrum of $CdMoO_4$ (Fig. 2f) takes advantage of the many previous vibrational studies on scheelite-type compounds [15–20], including a single crystal vibrational study [17]. The determination of the total modes, the identification of the different optical modes and the proposed

Table 3
Catalytic results of the mild oxidation of propene at 703 K

Catalyst	Conversion (%) for C_3H_6	Selectivity (%)			Balance
		Acrolein	Acetone	CO_2	
$CdWO_4$	2.2	17	3	78	2%
$CdMo_{0.125}W_{0.875}O_4$	12	12	2	80	6% (CO)
$CdMo_{0.25}W_{0.75}O_4$	16	14	1	67	18% (CO)
$CdMo_{0.5}W_{0.5}O_4$	1.1	32	6	58	4%
$CdMoO_4$	2.1	23	2	75	–

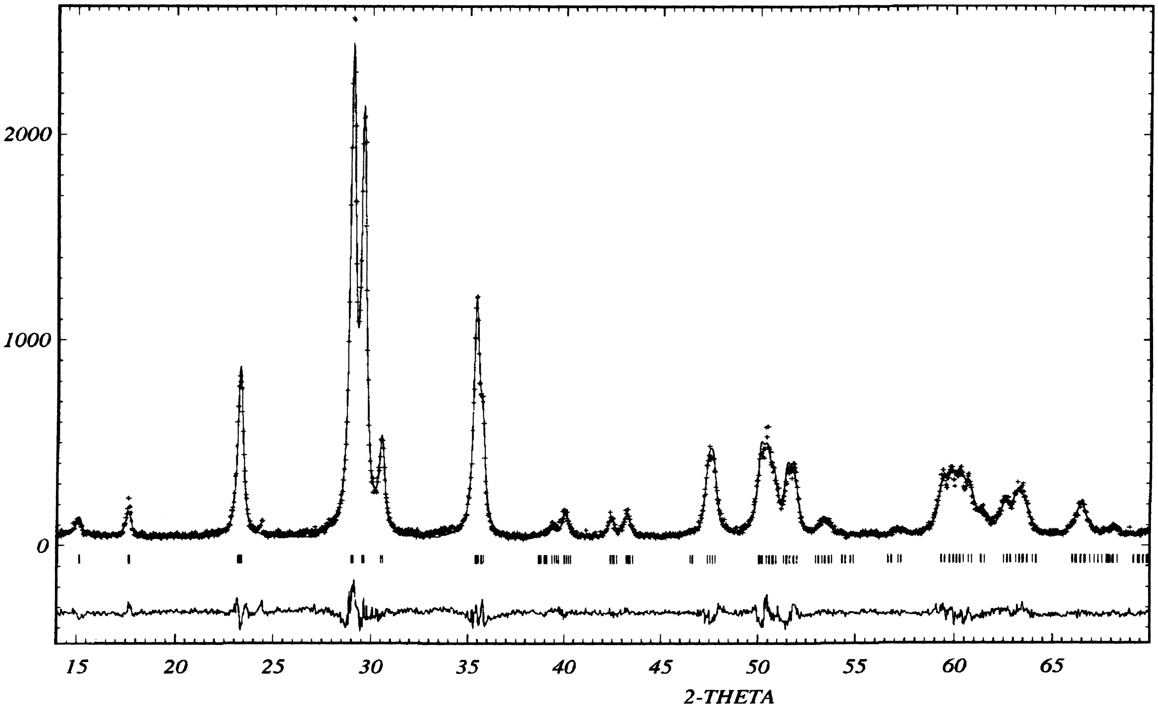


Fig. 1. Experimental (+), calculated (−) and difference XRD pattern, for the "pure" solid solution wolframite-type $CdMo_{0.25}W_{0.75}O_4$.

assignment agree with those previously given by Liegeosis-Duyckaerts and Tarte [15,16] and with the symmetries deduced from the reflection single crystal measurements of Barker [17]:

$$\Gamma_{opt} = 3A_g + 5B_g + 5A_u + 3B_u + 5E_g + 5E_u$$

The vibrational study confirms the spectrum forecasted for a tetrahedral coordination of molybdenum and a dodecahedral surrounding of cadmium.

The structure discussion of the wolframite-type materials (Fig. 2a–c) is based on Blasse assignments [21] and on our own calculations [22]

$$\Gamma_{opt} = 8A_g + 10B_g + 8A_u + 10B_u$$

Skeletal measurements confirm that the overall coordination around tungsten is 6, giving rise to ribbons of edge sharing distorted octahedra, that form a polymeric anionic structure with composition $[(W_2O_8)^{4-}]_n$, as shown in Fig. 3. Similarly, the coordination at cadmium is also 6 and gives rise to parallel ribbons of edge sharing distorted octahedra. It results that the overall coordination at tungsten is 6, even if a tetrahedral coordination has been taken as a good approximation, because two W–O bonds are very long. This last hypothesis is anyway rejected when we observe the Raman peaks present in the region 600–500 cm^{-1}, due to the forecasted vibrational modes for the octahedral configuration.

The substitution of W by Mo in the wolframite-type compounds (Fig. 2b and c) produces significant shifts of the IR bands; in particular, the ν_{as} stretch of the WO_2 terminal bonds is moved from 835 cm^{-1} for $CdWO_4$ to 809 cm^{-1} for $CdMo_{0.25}W_{0.75}O_4$ and correspondingly the ν_{as} stretch of the $[W_2O_4]_n$ chains moves from 595 to 573 cm^{-1}. This is due to the fact that tungsten is more electronegative than molybdenum, so W–O bonds are higher covalent with respect to Mo–O. As a result, the bond length is greater for Mo–O and the bond angle is compressed in the substituted compounds [22].

The IR spectrum of the scheelite-type $CdW_{1-x}Mo_x O_4$ solid solution (Fig. 2d and e) presents some definite differences with respect to that of $CdMoO_4$

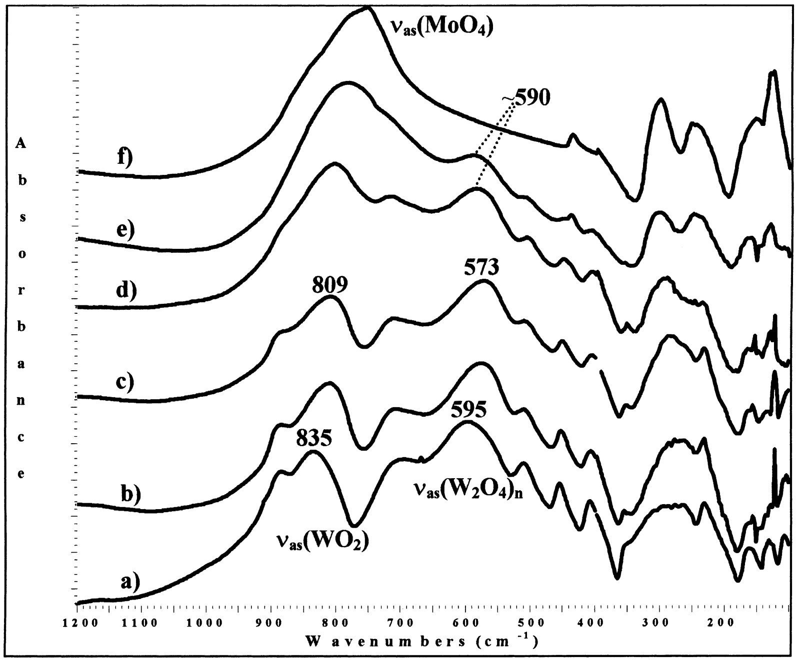


Fig. 2. FT-IR spectra of $CdMo_xW_{1-x}O_4$ powders: x=0 (a); x=0.125 (b); x=0.25 (c); x=0.5 (d); x=0.75 (e); x=1 (f).

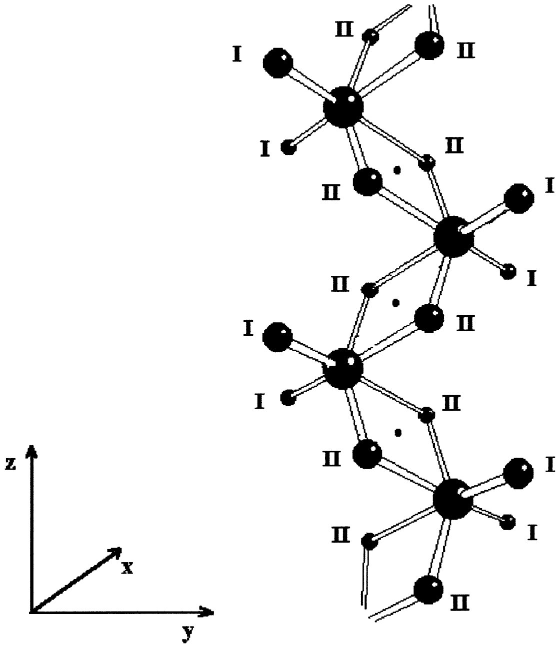
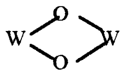


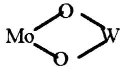
Fig. 3. View of the structure of the polymeric $[(W_2O_8)^{4-}]_n$ anion in the wolframite structure of $CdWO_4$. Bridging (II) and terminal (I) oxygens are distinct; the dots indicate inversion centres.

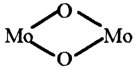
(Fig. 2f). The main maximum, assigned to the asymmetric stretching mode of the MoO_4 tetrahedra, shifts to higher frequency near 30 cm^{-1} by adding W, again in agreement with the stronger W–O bond. Moreover a new, broad component appears, near 590 cm^{-1}, possibly due to wolframite traces.

The Raman spectrum (not shown here) of the scheelite solid solution shows some additional components with respect to pure $CdMoO_4$. These features can be interpreted as arising from the splitting of the highest frequency Mo–O stretches, according to the appearance of W–O stretching modes.

4. Discussion

As we have seen in the first part of the results, $CdWO_4$, $CdMo_{0.5}W_{0.5}O_4$ and $CdMoO_4$ are almost inactive in propane conversion. Their activity in propene conversion is also very low. This can be explained in the case of $CdMoO_4$ by the fact that this compound contains isolated MoO_4 tetrahedra. The activity of $CdWO_4$ is also very low, although it contains infinite linear chains of WO_6 octahedra. Since the activity of MoO_3 [23,24], which also presents similar chains, is important in propylene oxidation, we conclude that W compounds are much less active than Mo ones, at least for such a structure type. The structure of $CdMo_{0.5}W_{0.5}O_4$ being quite similar to that of $CdMoO_4$ shows that isolated WO_4 tetrahedra are also inactive. On the contrary, the two other compounds $CdMo_{0.25}W_{0.75}O_4$ and $CdMo_{0.125}W_{0.875}O_4$ present the structure of $CdWO_4$, in which MoO_6 octahedra statistically replace WO_6 octahedra. Their activity is enhanced relative to that of $CdWO_4$, notably in propane conversion. However, their selectivity to mild oxygenation products is not so high as expected. This can be explained, in the case of propylene, by the high temperature used; in fact acrolein is not very stable under O_2 excess at 700 K. This activity can be related to the presence of MoO_6 octahedra: whereas 

entities in long chains seem to be little active, it appears that the presence of molybdenum 

or 

in these chains really modifies the activity. Unfortunately this mixed structure with infinite chains cannot contains more than 20–25% of Mo octahedra.

If we assume a transformation of propane into acrolein via propylene as intermediate, the results in Tables 2 and 3 show that the $CdMo_{0.25}W_{0.75}O_4$ and $CdMo_{0.125}W_{0.875}O_4$ solid solutions are active in propane ODHR but poorly selective in the oxidation of propylene into acrolein. This would explain why so low amounts of acrolein are obtained from propane oxidation.

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